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(71) Applicant: **EXXON CHEMICAL PATENTS INC.**
200 Park Avenue
Florham Park New Jersey 07932(US)

(72) Inventor: **Chang, Main**
15910 Dunmoor Drive
Houston Texas 77059(US)

(74) Representative: **Veldhuizen, Albert Dirk**
Willem et al
Exxon Chemical Limited Exxon Chemical
Technology Centre PO Box 1
Abingdon Oxfordshire OX13 6BB(GB)

(54) **Method for utilizing triethylaluminum to prepare an alumoxane support for an active metallocene catalyst.**

(57) This invention relates to a process for preparing a supported metallocene alumoxane catalyst for use in the polymerization of olefins. The invention particularly relates to the use of silica gel containing from about 6 to about 20 per cent by weight adsorbed water as the catalyst support material. It has been found that such silica gel may be safely added to an trialkyl aluminum solution, preferably a mixed trimethylaluminum-triethylaluminum solution, to form by direct reaction with the adsorbed water content of the silica gel catalyst support material the alumoxane component of the catalyst system. An alumoxane coated silica gel is formed to which a metallocene may be added and the resulting material dried to free flowing powder. The dry free flowing powder may then be used as a supported metallocene alumoxane catalyst complex for gas phase or liquid phase polymerization of olefins.

EP 0 367 503 A1

METHOD FOR UTILIZING TRIETHYLALUMINUM TO PREPARE AN ALUMOXANE SUPPORT FOR AN ACTIVE METALLOCENE CATALYST

Background of the Invention

1. Field of the Invention

5 This invention relates to a process for preparing a supported metallocene-alumoxane catalyst for use in the gas phase or liquid phase polymerization of olefins. The invention particularly relates to the use of silica gel containing from about 6 to about 20 per cent by weight adsorbed water as the catalyst support material. It has been found that such silica gel may be safely added to a mixed solution of trialkyl aluminums to form, 10 by direct reaction with the adsorbed water content of the silica gel, the alumoxane component of the catalyst system. In the present invention the alumoxane component is formed by contacting undehydrated silica gel with a mixed solution of triethylaluminum and triethylaluminum. A metallocene may be added to the alumoxane coated silica gel so formed and the resulting material dried to free flowing powder to yield a supported catalyst which is comparable in catalytic activity to a catalyst prepared solely with 15 methylaluminum as the alumoxane forming component.

2. Background to the Invention

20 Olefin polymerization catalysts comprising a metallocene and an aluminum alkyl component were first proposed in about 1956. Australian patent 220436 proposed for use as a polymerization catalyst a bis-(cyclopentadienyl) titanium, zirconium, or vanadium salt as reacted with a variety of halogenated or unhalogenated aluminum alkyl compounds. Although capable of catalyzing the polymerization of ethylene, such catalytic complexes, especially those made by reaction with a trialkyl aluminum, had an insufficient 25 level of catalytic activity to be employed commercially for production of polyethylene or copolymers of ethylene.

Later it was found that certain metallocenes such as bis-(cyclopentadienyl) titanium, or zirconium dialkyls in combination with aluminum alkyl/water cocatalyst formed catalyst systems for the polymerization of ethylene. Such catalysts are discussed in German Patent Application 2,608,863 which discloses a 30 polymerization catalyst for ethylene consisting of bis-(cyclopentadienyl) titanium dialkyl, trialkyl aluminum and water. German Patent Application 2,608,933 discloses an ethylene polymerization catalyst consisting of a cyclopentadienyl zirconium salt, a trialkyl aluminum cocatalyst and water. European Patent Application No. 0035242 discloses a process for preparing ethylene and atactic propylene polymers in the presence of a cyclopentadienyl transition metal salt and an alumoxane. Such catalysts have sufficient activity to be 35 commercially useful and enable the control of polyolefin molecular weight by means other than hydrogen addition -- such as by controlling the reaction temperature or by controlling the amount of cocatalyst alumoxane as such or as produced by the reaction of water with an aluminum alkyl.

To realize the benefits of such catalyst systems, one must use or produce the required alumoxane cocatalyst component. An alumoxane is produced by the reaction of an aluminum alkyl with water. The 40 reaction of an aluminum alkyl with water is very rapid and highly exothermic. Because of the extreme violence of the reaction the alumoxane cocatalyst component has, heretofore, been separately prepared by one of two general methods. Alumoxanes may be prepared by adding an extremely finely divided water, such as in the form of a humid solvent, to a solution of aluminum alkyl in benzene or other aromatic hydrocarbons. The production of an alumoxane by such procedure requires use of explosion-proof 45 equipment and very close control of the reaction conditions in order to reduce potential fire and explosion hazards. For this reason, it has been preferred to produce alumoxane by reacting an aluminum alkyl with a hydrated salt, such as hydrated copper sulfate. In such procedure a slurry of finely divided copper sulfate pentahydrate and toluene is formed and mantled under an inert gas. Aluminum alkyl is then slowly added to the slurry with stirring and the reaction mixture is maintained at room temperature for 24 to 48 hours during 50 which a slow hydrolysis occurs by which alumoxane is produced. Although the production of alumoxane by a hydrated salt method significantly reduces the explosion and fire hazard inherent in the wet solvent production method, production of an alumoxane by reaction with a hydrated salt must be carried out as a process separate from that of producing the metallocene-alumoxane catalyst itself, is slow, and produces hazardous wastes that create disposal problems. Further, before the alumoxane can be used for the

production of an active catalyst complex the hydrated salt reagent must be separated from the alumoxane to prevent it from becoming entrained in the catalyst complex and thus contaminating any polymer produced therewith.

U. S. Patent 4,431,788 discloses a process for producing a starch filled polyolefin composition wherein a trialkyl aluminum is first reacted with starch particles. The starch particles are then treated with a (cyclopentadienyl)-chromium, titanium, vanadium or zirconium alkyl to form a metallocene-alumoxane catalyst complex on the surface of the starch particles. An olefin is then polymerized about the starch particles by solution or suspension polymerization procedures to form a free-flowing composition of polyolefin-coated starch particles. German Patent 3,240,382 likewise discloses a method for producing a filled polyolefin composition which utilizes the water content of an inorganic filler material to directly react with a trialkyl aluminum and produce thereon an active metallocene alumoxane catalyst complex. Polymer is produced by solution or gas phase procedures at the filler surface to uniformly coat the filler particles and provide a filled polymer composition.

German Patent 3,240,382 notes that the activity of a metallocene-alumoxane catalyst is greatly impaired or lost when prepared as a surface coating on an inorganic material. Although German Patent 3,240,382 suggests that an inorganic material containing absorbed or adsorbed water may be used as a filler material from which the alumoxane cocatalyst component may be prepared by direct reaction with a trialkyl aluminum, the only water containing inorganic filler materials which are identified as capable of producing the alumoxane without adversely affecting the activity of the metallocene alumoxane catalyst complex are certain inorganic materials containing water of crystallization or bound water, such as gypsum or mica. German Patent 3,240,382 does not illustrate the production of a catalyst coated inorganic filler material wherein the inorganic material is one having absorbed or adsorbed water. Nor does German Patent 3,240,382 describe an inorganic filler material having absorbed or adsorbed water which has surface area or pore volume properties suitable for service as a catalyst support for a gas phase polymerization procedure.

My co-pending U.S. Patent Application Serial No. 134,413 discloses a method by which the requisite alumoxane cocatalyst component for a supported metallocene gas phase polymerization catalyst may be safely and economically prepared by addition of an "undehydrated" silica gel to a trialkyl aluminum solution. My co-pending application illustrates the production of highly active silica gel supported gas phase metallocene-alumoxane catalyst wherein trimethylaluminum is utilized to form the alumoxane. Although the reaction product of triethylaluminum with water is known to form an ineffective cocatalyst, a highly active catalyst system is formed in accordance with the method disclosed in my co-pending application Serial No. 134,413, by reacting triethylaluminum with undehydrated silica gel followed by reacting with metallocene.

Although the much lower cost of triethylaluminum (TEAL) compared to trimethylaluminum (TMA) would seem to make TEAL preferred for use, such is still not the case when viewed in light of the difference in catalyst activity between a TMA produced catalyst system compared to a TEAL produced catalyst system. The supported catalyst produced with TMA alone always has an activity at least about 20% greater than a like catalyst system produced with TEAL alone. More typically, the activity of a TMA produced catalyst may be about 100% greater than a TEAL produced catalyst. Hence, from a commercial production standpoint, the catalyst activity difference still dictates the use of TMA for production of the alumoxane cocatalyst component despite the cost savings that could be realized by use of TEAL as an alternative.

It would be desirable to devise an economical procedure whereby an active supported metallocene-alumoxane catalyst could be safely produced for use as a gas phase or high pressure polymerization catalyst. To be economical the procedure should dispense with the requirement of producing the alumoxane component as a separate component apart from the procedure by which the supported catalyst itself is prepared. Further, it would be desirable to devise a procedure which utilizes TEAL to produce a substantial portion of the alumoxane cocatalyst required to provide a supported metallocene-alumoxane catalyst of an activity comparable to one wherein the requisite alumoxane cocatalyst component is formed solely from TMA.

Summary of the Invention

The process of this invention utilizes as the catalyst support material silica particles having a surface area in the range of about 10 m²/g to about 700 m²/g, preferably about 100-500 m²/g and desirably about 200-400 m²/g, a pore volume of about 3 to about 0.5 cc/g and preferably 2-1 cc/g and an adsorbed water content of from about 6 to about 20 weight per cent, preferably from about 9 to about 15 weight per cent. Such silica particles are referred to hereafter as an "undehydrated silica gel." The term "undehydrated silica gel" is used herein to include gels which have a water content established by some drying or

hydroxon step but which have a level of water content similar to an undehydrated silica gel. The silica gel supported metallocene-alumoxane catalyst is prepared by adding the undehydrated silica gel to a stirred solution of trialkyl aluminum in an amount sufficient to provide a mole ratio of trialkyl aluminum to water of from about 3:1 to about 1:2, preferably 1.2:1 to about 0.8:1; thereafter adding to this stirred solution a
 5 metallocene in an amount sufficient to provide an aluminum to transitional metal ratio of from about 1000:1 to 1:1, preferably from about 300:1 to 10:1, most preferably from about 150:1 to about 30:1; removing the solvent and drying the solids to a free flowing powder. Drying can be obtained by modest heating or vacuum.

The dried free flowing powder comprises a metallocene-alumoxane catalyst complex adsorbed upon the
 10 surface of the silica gel support particles. The supported catalyst complex has an activity sufficient for use as a catalyst for polymerization of olefins by conventional gas phase or liquid phase polymerization procedures.

The process of this invention further provides for the use of TEAL to produce a substantial portion of the alumoxane cocatalyst component required to produce a supported metallocene-alumoxane catalyst
 15 having a degree of catalytic activity which is comparable to a catalyst of like composition wherein the alumoxane cocatalyst component is produced solely with TMA. Accordingly, in this embodiment of the process, the undehydrated silica gel support material is added to a stirred solution of TMA and TEAL, the mole ratio of TMA:TEAL in common solution being from about 0.3 to about 3.0 and the mole sum of TMA and TEAL being selected to provide a mole ratio of Al to transition metal in the final catalyst composition of
 20 from about 150:1 to about 30:1; thereafter the metallocene is added to the stirred solution after which the solvent is removed and the solids dried to a free-flowing powder. The supported catalyst metallocene-alumoxane so resulting has a catalyst activity at least comparable to a supported catalyst of like metallocene composition and Al:transition metal ratio the alumoxane component of which is produced solely from TMA.

Detailed Description of the Preferred Embodiments

The present invention is directed towards a method for preparing a supported catalyst system for use in
 30 the gas phase or liquid phase polymerization of olefins. The supported catalyst is particularly useful for the gas phase polymerization of ethylene to high molecular weight polyethylenes such as linear low density polyethylene (LLDPE) and high density polyethylene (HDPE). The polymers are intended for fabrication into articles by extrusion, injection molding, thermoforming, rotational molding, and the like. In particular, the polymers prepared with the catalyst complex and by the method of this invention are homopolymers of
 35 ethylene and copolymers of ethylene with higher alpha-olefins having from 3 to about 10 carbon atoms and preferably 4 to 8 carbon atoms. Illustrative of the higher alpha-olefins are butene-1, hexene-1, and octene-1.

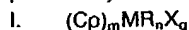
In the process of the present invention, ethylene, either alone or together with alpha-olefins having three or more carbon atoms, is polymerized in the presence of a silica gel supported catalyst system comprising at least one metallocene and an alumoxane.

40 In accordance with this invention, one can also produce olefin copolymers, particularly copolymers of ethylene and higher alpha-olefins having from 3-18 carbon atoms.

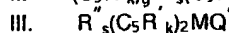
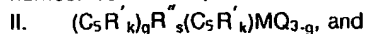
The active catalyst complex prepared by the process of this invention comprises a metallocene and an alumoxane formed onto the surface of a silica gel support material. Alumoxanes are oligomeric aluminum compounds represented by the general formula $(R-Al-O)_y$, which is believed to be a cyclic compound and $R-(R-Al-O)_y-AlR_2$, which is a linear compound. In the general formula, "R" is a C_1-C_{10} alkyl group such as, for
 45 example, methyl, ethyl, propyl, butyl, and pentyl and "y" is an integer from 2 to about 30 and represents the degree of oligomerization of the alumoxane. Preferably, the degree of oligomerization, "y," is about 4 to about 25 and most preferably 6-25. Generally, in the preparation of alumoxanes from, for example, the reaction of trimethyl aluminum and water, a mixture of linear and cyclic compounds is obtained. Generally,
 50 an alumoxane having a higher degree of oligomerization will, for a given metallocene, produce a catalyst complex of higher activity than will an alumoxane having a lower degree of oligomerization. Hence, the procedure by which alumoxane is produced by direct reaction of a trialkyl aluminum with an undehydrated silica gel should insure the conversion of the bulk quantity of the trialkyl aluminum to an alumoxane having a high degree of oligomerization. In accordance with this invention the desired degree of oligomerization is
 55 obtained by the order of addition of reactants as described hereinafter.

The metallocene may be any of the organometallic coordination compounds obtained as a cyclopentadienyl derivative of a transition metal. Metallocenes which are useful for preparing an active catalytic complex according to the process of this invention are the mono, bi and tri cyclopentadienyl or substituted

cyclopentadienyl metal compounds and most preferably, bi-cyclopentadienyl compounds. The metallocenes particularly useful in this invention are represented by the general formulas:



wherein Cp is a cyclopentadienyl ring, M is a Group 4b or 5b transition metal and preferably a Group 4b transition metal, R is a hydrocarbonyl group or hydrocarboxy group having from 1 to 20 carbon atoms, X is a halogen, and "m" is a whole number from 1 to 3, "n" is a whole number from 0 to 3, and "q" is a whole number from 0 to 3.



wherein $(C_5R'_k)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbonyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radicals containing from 1 to 20 carbon atoms, a silicon-containing hydrocarbonyl radical, or a hydrocarbonyl radical wherein two carbon atoms are joined together to form a C_4-C_6 ring, R'' is C_1-C_4 alkylene radical, a dialkyl germanium or silicone, or an alkyl phosphine or amine radical bridging two $(C_5R'_k)$ rings, Q is a hydrocarbonyl radical such as aryl, alkyl, alkenyl, alkylaryl, or arylalkyl having 1-20 carbon atoms, hydrocarboxy radical having 1-20 carbon atoms or halogen and can be the same or different, Q' is an alkylidene radical having from 1 to about 20 carbon atoms, s is 0 or 1, g is 0, 1 or 2; when g is 0, s is 0; k is 4 when s is 1 and k is 5 when s is 0 and M is as defined above.

Exemplary hydrocarbonyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl, and the like. Exemplary alkylene radicals are methylene, ethylene, propylene, and the like. Exemplary halogen atoms include chlorine, bromine and iodine and of these halogen atoms, chlorine is preferred. Exemplary of the alkylidene radicals is methylidene, ethylidene and propylidene.

Of the metallocenes, hafnocene, zirconocenes and titanocenes are most preferred. Illustrative but non-limiting examples of the metallocenes which can be usefully employed in accordance with this invention are monocyclopentadienyl titanocenes such as, cyclopentadienyl titanium trichloride, pentamethylcyclopentadienyl titanium trichloride; bis(cyclopentadienyl) titanium diphenyl; the carbene represented by the formula $Cp_2Ti=CH_2 \cdot Al(CH_3)_2Cl$ and derivatives of this reagent such as $Cp_2Ti=CH_2 \cdot Al(CH_3)_3$, $(Cp_2TiCH_2)_2$, $Cp_2TiCH_2CH(CH_3)CH_2$, $Cp_2Ti=CHCH_2CH_2$, $Cp_2Ti=CH_2 \cdot AlR'_2Cl$, wherein Cp is a cyclopentadienyl or substituted cyclopentadienyl radical, and R' is a alkyl, aryl, or alkylaryl radical having from 1-18 carbon atoms; substituted bis(Cp)Ti(IV) compounds such as bis(indenyl)Ti diphenyl or dichloride, bis-(methylcyclopentadienyl)Ti diphenyl or dihalides and other dihalide complexes; dialkyl, trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds such as bis(1,2-dimethylcyclopentadienyl)Ti diphenyl or dichloride, bis(1,2-diethylcyclopentadienyl)Ti diphenyl or dichloride and other dihalide complexes; silicone, phosphine, amine or carbon bridged cyclopentadiene complexes, such as dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride, methylenedicyclopentadienyl titanium diphenyl or dichloride and other dihalide complexes and the like.

Illustrative but non-limiting examples of the zirconocenes which can be usefully employed in accordance with this invention are, cyclopentadienyl zirconium trichloride, pentamethylcyclopentadienyl zirconium trichloride, bis(cyclopentadienyl) zirconium diphenyl, bis(cyclopentadienyl)zirconium dichloride, the alkyl substituted cyclopentadienes, such as bis(ethyl cyclopentadienyl)zirconium dimethyl, bis(β -phenylpropylcyclopentadienyl)zirconium dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, and dihalide complexes of the above; di-alkyl, tri-alkyl, tetra-alkyl, and penta-alkyl cyclopentadienes, such as bis-(pentamethylcyclopentadienyl)zirconium dimethyl, bis(1,2-dimethylcyclopentadienyl)zirconium dimethyl, bis-(1,3-diethyl-cyclopentadienyl)zirconium dimethyl and dihalide complexes of the above; silicone, phosphorus, and carbon bridged cyclopentadiene complexes such as dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide, methylphosphine dicyclopentadienyl zirconium dimethyl or dihalide, and methylene dicyclopentadienyl zirconium dimethyl or dihalide, carbenes represented by the formulae $Cp_2Zr=CH_2P(C_6H_5)_2CH_3$, and derivatives of these compounds such as $Cp_2ZrCH_2CH(CH_3)CH_2$.

Bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)-vanadium dichloride and the like are illustrative of other metallocenes.

Generally the use of a metallocene which comprises a bis(substituted cyclopentadienyl) zirconium will provide a catalyst complex of higher activity than a corresponding titanocene or a mono cyclopentadienyl metal compound. Hence bis(substituted cyclopentadienyl) zirconium compounds are preferred for use as the metallocene.

Heretofore the alumoxane component of the active catalyst complex has been separately prepared then added as such to a catalyst support material which is then treated with a metallocene to form the active catalyst complex. One procedure heretofore employed for preparing the alumoxane separately is that of

contacting water in the form of a moist solvent with a solution of trialkyl aluminum in a suitable organic solvent such as benzene or aromatic hydrocarbon. As before noted this procedure is attendant with fire and explosion hazards which requires the use of explosion-proof equipment and carefully controlled reaction conditions. In an alternative method heretofore employed for the separate production of alumoxane, an aluminum alkyl is contacted with a hydrated salt, such as hydrated copper sulfate. The method comprised treating a dilute solution of aluminum alkyl in, for example, toluene, with a copper sulfate pentahydrate. A slower, controlled hydrolysis of the aluminum alkyl to alumoxane results which substantially eliminates the fire and explosion hazard but with the disadvantage of the creation of hazardous waste products that must be disposed of and from which the alumoxane must be separated before it is suitable for use in the production of an active catalyst complex. Separate production of the alumoxane component by either procedure is time consuming and costly. Correspondingly, the use of a separately produced alumoxane greatly increases the cost of producing a metallocene-alumoxane catalyst.

In accordance with the present invention the alumoxane component of the catalyst complex is prepared by direct reaction of a trialkyl aluminum or trialkyl aluminum mixtures with the material utilized as the catalyst support, namely an undehydrated silica gel. Silica useful as the catalyst support is that which has a surface area in the range of about 10 to about 700 m²/g, preferably about 100-500 and desirably about 200-400 m²/g, a pore volume of about 3 to about 0.5 cc/g and preferably 2-1 cc/g, and an adsorbed water content of from about 6 to about 20 weight percent, preferably from about 9 to about 15 weight percent. The average particle size (APS) of the silica may be from about 0.3μ to about 100μ, and for a gas phase catalyst preferably from about 30μ to about 60μ (1μ = 10⁻⁶m). For a catalyst intended for high pressure polymerization the particle size of the silica should range from about 0.3 to no greater than about 10μ. Hereafter, silica having the above identified properties is referred to as undehydrated silica gel.

Undehydrated silica gel, as defined above, is added over time, about a few minutes, to a stirred solution of trialkyl aluminum, in an amount sufficient to provide a mole ratio of trialkyl aluminum to water of from about 3:1 to 1:2, preferably about 1.2:1 to 0.8:1. When used singularly the trialkyl aluminum preferred for use in forming the alumoxane is trimethylaluminum. Next in order of preference, when used singularly, is triethylaluminum. Although triethylaluminum when reacted with a moist solvent or a hydrated salt does not produce an alumoxane product which will serve as a cocatalyst for production of a high activity metallocene-alumoxane supported catalyst, it may be used in accordance with the procedure of this invention to produce an alumoxane coated silica particle to which a metallocene may be added to form a high activity metallocene-alumoxane supported catalyst. Hence, in the process of this invention, a high activity supported catalyst may be produced solely from TEAL, although a TEAL produced catalyst will generally have a lower degree of catalytic activity than a catalyst of similar composition the alumoxane cocatalyst of which is produced solely from TMA. The solvents used in the preparation of the catalyst system are inert hydrocarbons, in particular a hydrocarbon that is inert with respect to the catalyst system. Such solvents are well known and include, for example, isobutane, butane, pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane, toluene, xylene and the like. The less toxic aliphatic hydrocarbon solvent is preferred. Also suitable for use as the aluminum trialkyl are tripropyl aluminum, tri-n-butyl aluminum tri-isobutyl aluminum, tri(2-methylpentyl) aluminum, trihexyl aluminum, tri-n-octyl aluminum, and tri-n-decyl aluminum. Although such trialkyl aluminum compounds are ineffective when used to form an alumoxane cocatalyst separately from the silica gel support material, when reacted with an undehydrated silica gel in accordance with the procedure of the invention an effective alumoxane cocatalyst component is formed as a coating on the silica gel particle. Again, in comparison to an alumoxane produced from TMA, the alternative trialkyl aluminum compounds will not, when used singularly, produce a catalyst which is as active as one produced solely from TMA.

Upon addition of the undehydrated silica gel to the solution of trialkyl aluminum, the water content of the silica gel controllably reacts with the trialkyl aluminum to produce an alumoxane which is deposited onto the surface of the silica gel particles. Although the reaction of the trialkyl aluminum with the water content of the silica gel proceeds relatively quickly, that is, it is generally completed within the time of about 5 minutes, it does not occur with the explosive quickness of that which occurs with free water. The reaction may be safely conducted in conventional mixing equipment under a mantle of inert gas.

Thereafter a metallocene is added to the stirred suspension of alumoxane silica gel product in an amount sufficient to provide a mole ratio of aluminum to transition metal of from about 1000:1 to about 1:1, preferably from about 300:1 to about 10:1 and most preferably from about 150:1 to about 30:1. The mixture is stirred for about 30 minutes to about one hour at ambient or an elevated temperature to permit the metallocene to undergo complete reaction with the adsorbed alumoxane. Thereafter, the solvent is removed and the residual solids are dried, preferably at a temperature of 25°C or greater, to a free flowing powder. The free flowing powder comprises a silica gel supported metallocene-alumoxane catalyst complex of

sufficiently high catalytic activity for use in the polymerization of olefins by conventional gas phase or liquid phase polymerization procedures.

The order of addition between the undehydrate silica gel and the trialkyl aluminum is important with regards to the activity of the supported catalyst which results upon addition of the metallocene. A supported catalyst composition of little or no activity results wherein an trialkyl aluminum is added to a stirred solvent suspension of undehydrated silica gel. It has been found that to prepare a supported catalyst composition of acceptable or high activity the order of mixing must be on wherein the undehydrated silica gel is added to a stirred solution of the trialkyl aluminum. It is believed that this order of mixing forces the trialkyl aluminum to undergo reaction in the context of a transient localized excess of trialkyl aluminum compared to a transient localized deficiency of water. Under a mixing condition which slowly adds undehydrated silica gel to a stirred solution of trialkyl aluminum, the bulk content of the trialkyl aluminum converts to an alumoxane with a degree of oligomerization of about 6-25 ($y = 6-25$). Production of an alumoxane with this degree of oligomerization results in a final metallocene alumoxane catalyst complex of useful or high activity. A reverse order of mixing, that is, addition of an trialkyl aluminum to a stirred solvent suspension of undehydrated silica gel yields a catalyst which has a low degree of catalytic activity.

In addition to the importance of proper mixing order in achieving a supported catalyst of useful activity, it has also been observed that the water content of the undehydrated silica gel influences final catalyst activity. Hence the undehydrated silica gel should have an adsorbed water content of from about 6 to about 20 weight percent. Preferably the adsorbed water content should be from about 9 to about 15 weight percent.

Further influencing the degree of activity attained in the final supported catalyst complex is the mole ratio of trialkyl aluminum to the adsorbed water content of the undehydrated silica gel. The quantities of trialkyl aluminum employed should, in comparison to the quantity of undehydrated silica gel of specified adsorbed water content, be selected to provide a mole ratio of total trialkyl aluminum to water of from about 3:1 to about 1:2, preferably from about 1.5:1 to about 0.8:1, more preferably from about 1.2:1 to about 0.8:1. It has been observed that for a given metallocene, a maximum catalyst activity is generally observed in the trialkyl aluminum to water mole ratio range of about 1.2:1 to about 0.8:1. Depending upon the particular trialkyl aluminum selected for use, commercially acceptable catalyst activities are exhibited in the trialkyl aluminum to water mole ratio range of about 3:1 to about 1:2.

Also influencing the cost of production and the level of catalytic activity obtained in the final supported catalyst complex is the mole ratio of aluminum to transition metal of the metallocene component. The quantity of metallocene added to the alumoxane adsorbed silica gel solids should be selected to provide an aluminum to transition metal mole ratio of from about 1000:1 to about 1:1, preferably from about 300:1 to about 10:1, and most preferably from about 150:1 to about 30:1. From the standpoint of economic considerations it is desirable to operate in the lower ranges of the aluminum to transition metal mole ratio in order to minimize the cost of catalyst production. The procedure of this invention is one which provides the maximum conversion of the trialkyl aluminum component to the most efficacious form of alumoxane, hence permits the safe production of a supported metallocene alumoxane catalyst of useful activity with minimum quantities of the costly trialkyl aluminum component.

As before noted, the type of trialkyl aluminum utilized for production of the alumoxane cocatalyst component exerts an influence over the degree of catalytic activity that can be achieved in the final catalyst composition. Heretofore trimethylaluminum has been the trialkyl aluminum of preference since it yields methylalumoxane (MAO). Metallocenes cocatalyzed with methylalumoxane exhibit substantially greater catalytic activities than when cocatalyzed with higher alkylalumoxanes such as ethylalumoxane. Thus, even though trimethylaluminum costs about ten times more than triethylaluminum, though desirable from a cost standpoint, because of its associated lower ability to activate the catalyst composition TEAL has not been the trialkyl aluminum of choice for use.

The present invention now provides a method by which substantial quantities of TEAL can be used in replacement of the more expensive TMA to produce a methyl alumoxane-ethylalumoxane mixed cocatalyst component which, when combined with a metallocene, produces a final supported catalyst having a degree of catalytic activity comparable to one of like Al:transition metal ratio and metallocene composition but which is cocatalyzed solely with methylalumoxane. In this embodiment of the invention, the trialkyl aluminum solution to which the undehydrated silica gel is added comprises a mixed solution of TMA and TEAL, in mole ratio of TMA:TEAL of from about 0.3 to about 3.0, in quantities to provide the quantity of total aluminum necessary to achieve the mole ratio of Al to transition metal desired in the final supported catalyst composition.

According to the invented procedure, a catalyst composition the alumoxane cocatalyst of which is produced solely from TMA generally has a catalytic activity (measured as g polymer/g transition metal/hr)

about twice as great as a catalyst of similar composition the cocatalyst alumoxane of which is produced solely from TEAL. In accordance with the method of this invention, a 1:1 mole ratio mixture of TMA to TEAL has been found to produce a silica gel supported mixed methyl alumoxane-ethyl alumoxane cocatalyst component which has substantially the same or greater degree of ability to promote catalytic activity by the metallocene component as does methylalumoxane alone. A 1:3 mole ratio mixture of TMA to TEAL has been found to produce a mixed methyl-ethyl alumoxane silica gel supported cocatalyst component which has about 85% of the activating ability of methylalumoxane to promote catalytic activity by the metallocene component.

By appropriate selection of the type and relative amounts of the metallocene and the trialkyl aluminum cocatalyst precursor, one can attain by the present method the particular active catalyst complex desired for any particular application. For example, higher concentrations of alumoxane in the catalyst system generally result in higher molecular weight polymer product. Therefore, when it is desired to produce a high molecular weight polymer a higher concentration of trialkyl aluminum is used, relative to the metallocene, than when it is desired to produce a lower molecular weight material. For most applications the ratio of aluminum in the aluminum alkyl to total metal in the metallocene can be in the range of from about 300:1 to about 20:1, and preferably about 200:1 to about 50:1.

Following the addition of the metallocene to the alumoxane adsorbed on the silica gel solids, the catalyst is dried to a free flowing powder. Drying of the catalyst may be conducted by filtration or evaporation of solvent at a temperature up to about 85°C. The dried free flowing powder comprises a metallocene-alumoxane complex adsorbed upon the surface of the silica gel support particles. The dried state composition exhibits a level of catalytic activity useful for polymerization of olefins by a gas phase or liquid phase procedure as are known in the art.

As disclosed in copending application Serial No. 728,111 filed April 29, 1985, the molecular weight of the polymer product can be controlled by the judicious selection of substituents on the cyclopentadienyl ring and use of ligands for the metallocene. Further, the comonomer content can be controlled by the judicious selection of the metallocene. Hence, by the selection of catalyst components it is possible to tailor the polymer product with respect to molecular weight and density. Further, one may tailor the polymerization reaction conditions over a wide range of conditions for the production of polymers having particular properties.

In the examples following, the melt index (MI) and melt index ratio (MIR) were determined in accordance with ASTM test D1238.

Example 1

300 ml of dried and degassed heptane is charged into a one-liter three-neck flask equipped with a magnetic stirring bar. A mixture of 80 ml of TMA in heptane (1.62 M) and 180 ml of TEAL in heptane solution (1.54 M) is then charged into the flask to form a clear solution. Thereafter, 100 g of "undehydrated" silica gel (Davison 948) which contains 8.1% of water is slowly added into the flask. After the addition is completed, the mixture is stirred at ambient temperature for one hour. Thereafter, 2.5 g of di-(n-butylcyclopentadienyl) zirconium dichloride slurried in 120 ml of heptane is then added into the flask and the mixture is allowed to react at ambient temperature for 30 minutes. The mixture in the flask is heated to 55°C in an oil bath while a nitrogen gas is purged through the flask to remove the solvent. The heating and nitrogen purging are stopped when the mixture in the flask turns into a solid form. The mixture is then dried under vacuum to form a free-flowing powder.

Example 2

The procedure of Example 1 is followed with the exception that a mixture with 10 ml of TMA in heptane (1.62 M) and 120 ml of TEAL in heptane solution (1.54 M) is added into the flask.

Example 3

The procedure of Example 1 is followed with the exception that a mixture with 30 ml of TMA in heptane (1.62 M) and 100 ml of TEAL in heptane solution (1.54 M) is added into the flask.

Example 4

The procedure of Example 1 is followed with the exception that a mixture with 65 ml of TMA in heptane (1.62 M) and 65 ml of TEAL in heptane solution (1.54 M) is added into the flask.

Example 5 (Comparative)

The procedure of Example 1 is followed with the exception that 130 ml of TMA in heptane solution (1.62 M) is added into the flask and the drying temperature is 75° C.

Example 6 (Comparative)

The procedure of Example 1 is followed with the exception that 130 ml of TEA in heptane solution (1.54 M) is added into the flask.

Catalyst Test

The activity of the catalyst powders of Examples 1-6 were determined at ambient temperature and 5 psig ethylene pressure by the following procedure. A 150 milliliter vial was freshly cleaned, heated to 130° C for 6 hours, cooled to room temperature and flushed with nitrogen for 10 minutes. The vial was provided with a magnetic stirring bar and 2.5 grams of catalyst composition was charged into the vial. At ambient temperature ethylene gas was fed into the vial and an ethylene pressure of 5 pig was maintained for one hour. Thereafter ethylene gas was vented from the vial and the polyethylene formed inside the vial was collected and weighed. The yield of polyethylene obtained with each catalyst composition is reported in Table I.

TABLE I

CATALYST TEST RESULT	
Catalyst	Amount Polyethylene Formed, g
Example 1	2.5
2	1.3
3	2.6
4	3.6
5	3.3
6	1.5

The invention has been described with reference to its preferred embodiments. From this description, a person of ordinary skill in the art may appreciate changes that could be made in the invention which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

Claims

1. A process for preparing a supported metallocene alumoxane catalyst for polymerization of olefins, comprising the steps of:

(a) adding undehydrated silica gel to a stirred solution containing trimethylaluminum (TMA) and triethylaluminum (TEAL) in a mole ratio of TMA:TEAL of from 0.3:1 to 3:1 and in amounts sufficient to provide a mole ratio of total trialkyl aluminum to water of from 3:1 to 1:2 and allowing the mixture to react;

(b) adding a metallocene to the reacted mixture;

(c) removing the solvent;

(d) drying the solids to a free flowing powder.

2. Process according to claim 1, wherein said undehydrated silica gel has a water content of from 6 to 20 weight percent.

5 3. Process according to claim 1 or claim 2, wherein the mole ratio of aluminum to transition metal in said metallocene is from 1000:1 to 1:1 and preferably from 300:1 to 10:1 and especially from 150:1 to 30:1.

4. Process according to any of the preceding claims, wherein said undehydrated silica gel has a water content of from 6 to 20 weight percent and/or the mole ratio of total trialkyl aluminum to water is from 1.2:1 to 0.8:1.

10 5. The process according to any of the preceding claims, wherein said undehydrated silica gel has a surface area of from 200 to 400 m²/g; a pore volume of from 1 to 2 cc/g and/or a particle size of from 30μ to 60μ.

6. A process for preparing a supported metallocene alumoxane catalyst for polymerization of ethylene and other alpha olefin monomers, comprising the steps of:

15 (a) adding undehydrated silica gel to a stirred solution containing trimethylaluminum (TMA) and triethylaluminum (TEAL) in a mole ratio of TMA:TEAL of from 0.3:1 to 3:1 and in amounts sufficient to provide a mole ratio of total trialkyl aluminum to water of from 3:1 to 1:2 and allowing the mixture to react;

(b) adding to the reaction mixture a metallocene of the formula: (Cp)_mMR_nX_q wherein Cp is a cyclopentadienyl ring, M is a Group 4b or 5b transition metal, R is a hydrocarbyl group or hydrocarboxy group having from 1 to 20 carbon atoms, X is a halogen, and m is a whole number from 1 to 3, n is a whole number from 0 to 3, and q is a whole number from 0 to 3;

(C₅R'_k)_gR''_s(C₅R'_k)MQ_{3-g}, or R''_s(C₅R'_k)₂MQ'

25 wherein (C₅R'_k) is a cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbyl radical containing from 1 to 20 carbon atoms, a silicon-containing hydrocarbyl radical, or a hydrocarbyl radical wherein two carbon atoms are joined together to form a C₄-C₆ ring, R'' is C₁-C₄ alkylene radical, a dialkyl germanium or silicone, or an alkyl phosphine or amine radical bridging two (C₅R'_k) rings, Q is a hydrocarbyl radical having 1-20 carbon atoms, hydrocarboxy radical having 1-20 carbon atoms or halogen and can be the same or different, Q' is an alkylidene radical having from 1 to about 20 carbon atoms, s is 0 or 1, g is 0, 1 or 2; when g is 0, s is 0; k is 4 when s is 1 and k is 5 when s is 30 0 and M is as defined above;

(c) removing the solvent;

(d) drying the solids to a free flowing powder.

7. Process according to claim 6, wherein said metallocene is a zirconocene or titanocene.

8. Process according to claim 7, wherein said zirconocene is selected from the group consisting of 35 cyclopentadienyl zirconium trichloride;

pentamethylcyclopentadienyl zirconium trichloride;

bis(cyclopentadienyl)zirconium diphenyl;

bis(cyclopentadienyl)zirconium dichloride; alkyl substituted cyclopentadienes, and their dihalide complexes;

40 dialkyl, trialkyl, tetra-alkyl, and penta-alkyl cyclopentadienes, and their dihalide complexes; and silicone, phosphorus, and carbon bridged cyclopentadiene complexes and wherein said titanocene is selected from the group consisting of monocyclopentadienyl titanocenes;

bis(cyclopentadienyl) titanium diphenyl; carbenes represented by the formula Cp₂Ti=CH₂ * Al(CH₃)₂Cl and their derivatives, wherein Cp is a cyclopentadienyl or substituted cyclopentadienyl radical; substituted bis-

45 (Cp)Ti(IV) compounds and their dihalide complexes; dialkyl, trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds and their dihalide complexes; and silicone, phosphine, amine or carbon bridged cyclopentadiene complexes, and their dihalide complexes.

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EUROPEAN SEARCH REPORT

Application Number

EP 89 31 1067

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 336 593 (EXXON) * Claims 1,8 * ---	1	C 08 F 4/642
A	EP-A-0 170 059 (HOECHST) * Claims * ---	1	
A	DE-A-3 240 382 (HOECHST) * Claims * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-02-1990	Examiner DE ROECK R.G.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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